



Photocatalytic degradation of Allura red and Quinoline yellow with Polyaniline/TiO₂ nanocomposite

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ABSTRACT

A series of polyaniline/TiO₂ (PANI/TiO₂) composites has been prepared from aniline and TiO₂ under various polymerization conditions. Among these conditions are the concentrations of aniline, ammonium persulfate, HCl, sodium dodecyl sulfate, and the amount of TiO₂. More composites were obtained by replacing HCl with H₂SO₄, H₃PO₄, and HNO₃ as dopant acids. Scanning electron microscopy, UV/vis-diffuse reflectance spectroscopy, FTIR and TGA were used to characterize some of these composites. The rate of degradation of dyes with these composites followed first-order kinetics in the dye concentration. The activity of the composite towards the degradation process differs according to the experimental polymerization conditions. The activity increased with the increase in the concentration of aniline monomer and persulfate, but decreased with increasing the concentration of HCl, sodium dodecyl sulfate, and the amount of TiO₂. The activity of composites formed in the presence of different acids followed the order H₂SO₄ > H₃PO₄ > HCl > HNO₃. The rate of composite/dye interaction was enhanced with the UV-irradiation, increasing load of composite, and temperature. It was retarded with the increase in initial dye concentration and pH. The activation parameters were determined and a plausible mechanism was proposed.

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1. Introduction

The textile and food industries use organic dyes which represent an important source of environmental contamination. Most of dyes are toxic on aquatic creatures and have carcinogenic effects on humans [1,2]. Allura red (ALR) is an azo dye used in foods, and cosmetics. Quinoline yellow (QY) is also another food colorant. Different techniques such as adsorption, oxidation, reduction, electrochemical and membrane filtration are applied to remove these pollutants from the industrial effluents. Oxidation processes are widely used both in industrial preparations and in environmental treatments [3,4]. An alternative and conventional method called the advanced oxidation processes (AOPs) based on the *in situ* generation of reactive OH• radical is applied. This radical species can quickly and nonselectively oxidize broad range of organic pollutants [5,6]. Most of AOPs comprise the combination of UV-light with H₂O₂, TiO₂, and O₃ [7].

Heterogeneous-conducting polymer composites have drawn the attention over the past few years [8]. Polyaniline (PANI) is one of these polymers that has attracted considerable attention for the

preparation of its composites with inorganic particles to improve its activity. Among these particles are BaTiO₃ [9], Mo₂SO₃ [10], V₂O₅ [11], ZrO₂ [12], MnO₂ [13], TiO₂ [14,15], and clay [16].

In addition to the electrical conductivity applications of polyaniline composites, most recent literature data concerning their catalytic activity towards the decolorization of organic dyes are available [13]. PANI/MnO₂ composite was used as a catalyst in the oxidative degradation of some organic dyes with H₂O₂. The reaction involved a catalytic action of the PANI counterpart of the composite towards H₂O₂ decomposition, which led to an additional generation of OH• radicals that are responsible for the degradation process. Wang and Min [17] have pointed out that PANI/TiO₂ photocatalyst plays an efficient role for the degradation of the dye methylene blue over that of free TiO₂. This behavior is owing to the ability of PANI to sensitize TiO₂ by absorbing both ultraviolet and visible light (190–800 nm), whereas the pure TiO₂ only absorbs ultraviolet light (λ < 380 nm). Therefore, if both the PANI/TiO₂-dye and TiO₂-dye systems are irradiated by natural light the former exhibits superior photocatalytic activity for the degradation of dye over the latter one. Similar behavior was obtained by Li and coworkers [18] on using a PANI/TiO₂ composite sample prepared via self assembling and graft polymerization for degradation of methyl orange under sunlight. They concluded that the PANI/TiO₂ composite modified with aminopropylsilane exhibits better photocatalytic activity compared with the neat-TiO₂

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due to the sensitizing effect of PANI. As the PANI/TiO₂ composite combines the properties that are difficult to attain separately with its individual components, i.e., the UV-sensitivity of anatase TiO₂ and the electrical conductivity of PANI, it has potential applications in diverse areas. Among these applications are the photocatalysis [17,19–21], solar cells [22], rechargeable batteries [23], gas sensing [24] and corrosion [25].

In the present paper, several kinds of PANI/TiO₂ composites have been synthesized under various polymerization conditions. Effects of their composition characteristics and the composite/dye operating conditions on the degradation rates of the title dyes were then investigated.

2. Experimental

2.1. Materials

Aniline (ANi) (Loba Chemie PVT, Mumbai, India) was distilled twice under reduced pressure and stored in the dark below 4 °C. TiO₂ (anatase, Aldrich) was used as received. Ammonium persulfate (APS), HasHmzel Laboratories Ltd. (Netherlands) was used as an oxidant. Allura red (ALR), Waker Chemical Products (France), C.I. 16035 (IUPAC name: disodium salt of 6-hydroxy-5-(2-methoxy-5-methyl-4-sulfophenyl) azo-2-naphthalene sulfonic acid) and Quinoline yellow (QY), Aldrich, C.I. 47005 (disodium salt of disulfonates of 2-(2-quinolyl)-1,3-indandione), Scheme 1, were used without prior purification. Their solutions were freshly prepared in twice distilled water. All other reagents were of high grade quality.

2.2. Instruments

Particle size and morphology of the composite have been examined by scanning electron microscope (SEM), Hitachi FL-SEM S-800. The sample was fixed on a SEM stage using carbon tapes and the measurements were done after deposition of thin Pt layer using an ion sputter (Hitachi E-1030). The infrared spectra were recorded on FTIR spectrophotometer (Perkin-Elmer 1430) using the KBr technique. The thermogravimetric analysis (TGA) was carried out using a Shimadzu TGA-50 thermogravimetric analyzer within 25–600 °C range at heating rate 10 °C/min in N₂ atmosphere. A computerized Shimadzu UV/Vis-2100S double beam recording spectrophotometer linked to an electronic temperature controller (TCC-260) was used for measuring the kinetics of dye disappearance via recording the spectra over the wavelength range 200–700 nm during the reaction progress. Calibration plots based on Beer–Lambert's law relating the absorbance to the concentration were established at the maximum absorbance of 502 and 414 nm for ALR and QY, respectively. Diffuse reflectance spectra have been recorded using an integrating sphere and BaSO₄ as a white standard. A UV-C tube lamp (15 W, length 41 cm, diameter 2.5 cm), model G15T8 (Philips, Holland) was used as the radiation source ($\lambda = 254$ nm). The pH measurements were carried out with a

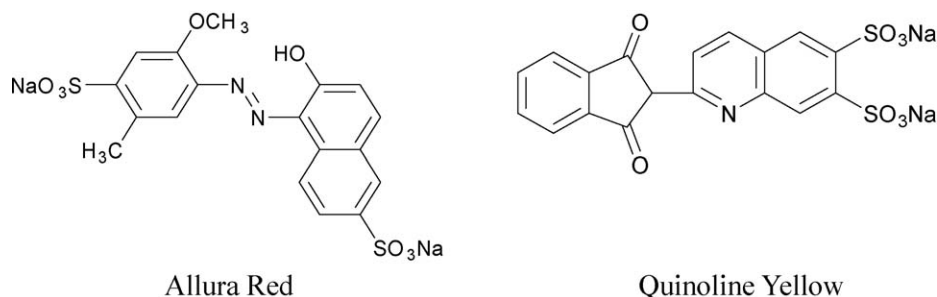
digital pH-meter (Fisher Scientific, USA, Model Accumet 825) equipped with a glass electrode. A shaker water thermostat (Julabo SW20C) was used to shake the heterogeneous reaction mixture at 150 rpm at fixed temperature ± 0.1 °C.

2.3. Preparation of PANI/TiO₂ nanocomposites

The composites were prepared by *in situ* suspension oxidative polymerization of aniline in the presence of TiO₂ in aqueous solution. A typical composite sample was prepared as follows: 1 ml of aniline was transferred dropwise into a beaker (400 ml) containing 190 ml of 1.26 M HCl (or H₂SO₄, H₃PO₄, HNO₃), APS (2.5 g, 0.058 M) and TiO₂ (1.0 g). The polymerization was allowed to proceed for 1 h at 25 °C with constant stirring using conventional magnetic stirrer. The green water dispersed material produced was then filtered under gravity through a filter paper and washed repeatedly with a large amount of doubly distilled water until the filtrate became colorless. It was then dried overnight in an oven at 60 °C to give white green material. The obtained material is a PANI/TiO₂ composite in its emeraldine salt state (CES), doped with HCl or any one of the above acids. For the composites prepared in the presence of surfactant (sodium dodecyl sulfate, SDS) the required amount of SDS was added prior to the addition of aniline. All the composites prepared under several experimental conditions are given in Table 2. The free HCl-doped PANI sample was prepared under the same procedure except that TiO₂ was not added.

2.4. Kinetic measurements

In a typical kinetics experiment, a number of open Pyrex beakers (100 ml) containing the solid composite (0.05 g) and water (20 ml) were placed adjacently as one row in the water shaker thermostat to attain the desired temperature. Above the reaction vessels was the UV-lamp extending horizontally at a distance of 14 cm from the surface of the solution to illuminate the reaction mixtures equally with the UV-light. The pre-thermostatted dye solution (5 ml) of the requisite concentration was then added to each beaker to start the reaction and the time was noted. All mixtures were immediately shaken with simultaneous illumination. The lamp was turned on 15 min prior to the reaction in order to attain constant output of light intensity. The photocatalytic reactions were carried out under atmospheric conditions where the irradiation source and the water thermostat were assembled inside a shelter to avoid the UV-radiation, Fig. 1. For spectrophotometric measurements the beakers were successively removed at different times of illumination. Since the solid composite sediments, it was quickly separated from the dye solution by filtration to quench the reaction. The filtrate was then transferred into a 1-cm quartz cell to measure its optical density at λ_{max} 502 and 414 nm for ALR and QY, respectively. The reaction was taken place to at least 75% completion in the presence of UV-light unless where otherwise stated. In the absence of the



Scheme 1.

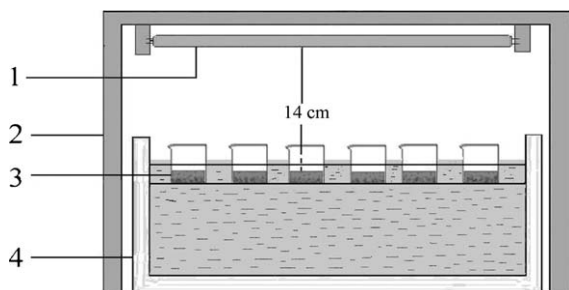


Fig. 1. Photoreactor setup. (1) UV-lamp, (2) UV-shelter, (3) reaction vessel and (4) water shaker thermostat.

composite, no change in the absorbance of each illuminated dye solution was observed, indicating the stability of the dyes against UV-light. The observed rate constant (k_o) was determined under various experimental conditions from the slope of the linear regression plot between $\ln(\text{absorbance})$ vs. time, which verifies the integrated first-order rate equation. $\ln A_t = \ln A_o - k_o t$. The specific rate constant (k) per gram dry composite (pgdc) was determined from the relation $k_o = km$, where m is the mass of the composite involved in the reaction with the dye.

3. Results and discussion

3.1. Characterization of the composites

3.1.1. Scanning electron microscopy

The SEM image of the free TiO_2 nanoparticles is shown in Fig. 2a. The TiO_2 nanoparticles are aggregated in aqueous solution in an irregular shape due to their high surface energy. Different appearance was observed for the PANI/ TiO_2 , Fig. 2b. Adsorption of PANI on the surface of TiO_2 nanoparticles leads to core-shell structures or PANI-coated TiO_2 nanoparticles. These composite nanoparticles grow in size via their binding by PANI chains to form multiparticles aggregates, which heap tightly than free TiO_2 nanoparticles [23]. Further evidence for the core-shell structure of PANI/ TiO_2 was reported by Xu et al. [26]. At high TiO_2 content (50 and 80 wt%) the composite present as particles, indicating the nucleus effect of TiO_2 nanoparticles on the polymerization of aniline. This results in a homogeneous PANI shell around the TiO_2 nanoparticles. Such conclusion supports our findings, particularly the present composite samples contain TiO_2 within the range 50–87 wt%, Table 2.

3.1.2. UV/vis-diffuse reflectance spectroscopy (DRS)

The UV/vis-diffuse reflectance spectra of TiO_2 and PANI/ TiO_2 composite are depicted in Fig. 3. Both the TiO_2 and PANI/ TiO_2 absorb light below 400 nm. Above this wavelength only the composite absorbs light giving rise to a peak at 440 nm and a broad peak in the range 500–750 nm, indicating the presence of the PANI on the surface of TiO_2 nanoparticles. Similar behaviors were observed by Wang and Min [17] and Min et al. [23]. Min et al. not only depended on their UV/vis-diffuse spectral results but also measured the ESR spectra for the free TiO_2 , PANI, and PANI/ TiO_2 composite. They concluded the existence of PANI on the surface of TiO_2 .

3.1.3. FTIR spectra

The FTIR spectra of the neat- TiO_2 , free polyaniline, and PANI/ TiO_2 composite are shown in Fig. 4. The main characteristic peaks of the polyaniline are assigned as follows: the band at 3488 cm^{-1} is attributed to N–H stretching mode [27]. The C=N and C=C stretching of the quinonoid and benzenoid units occur at 1579 and 1488 cm^{-1} . Bands at 1299 and 1240 cm^{-1} are assigned to the C–N

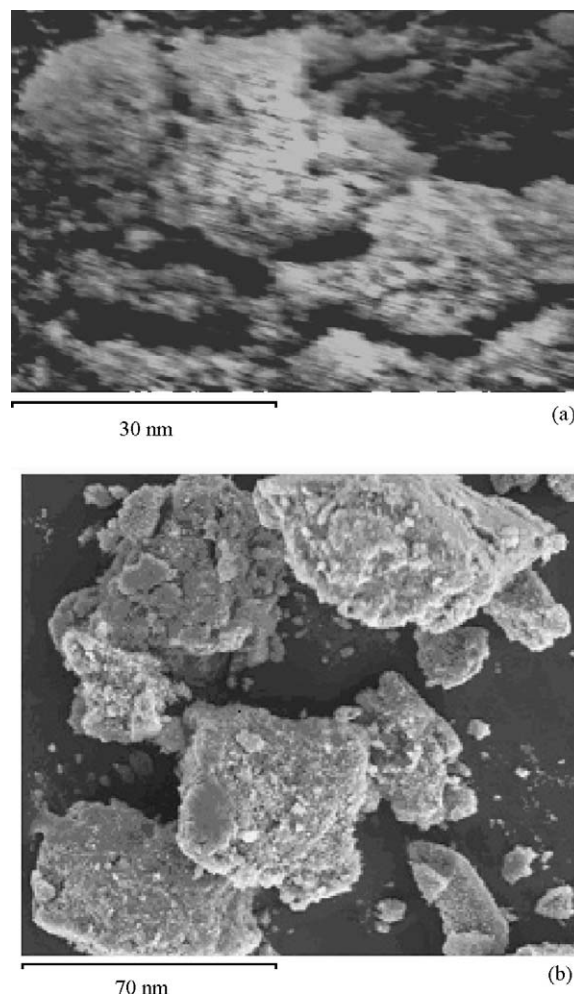


Fig. 2. Scanning electron micrographs (SEM). (a) Free TiO_2 particles and (b) PANI/ TiO_2 composite (II).

stretching of benzenoid unit while the band at 1134 cm^{-1} is due to the quinonoid unit of doped PANI. The peak at 809 cm^{-1} is associated with C–C and C–H for benzenoid unit. The peaks of TiO_2 at 1022 and 406 cm^{-1} were also found in the spectrum of PANI/ TiO_2 composite. The peaks of PANI around 1299, 1488 and 1578 cm^{-1} corresponding to the stretching mode of C–N and C=N denote the formation of leucomeraldine and peringraniline forms

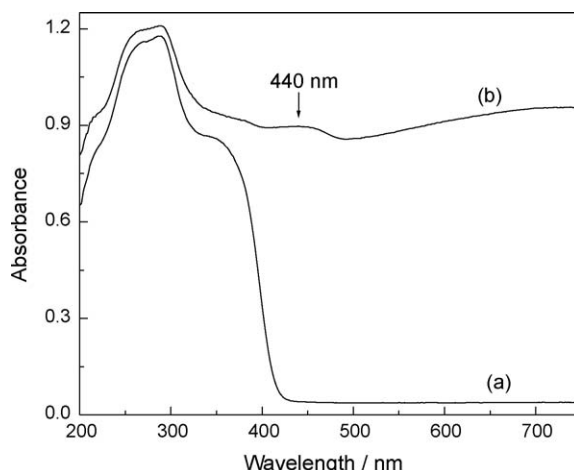


Fig. 3. Diffuse reflectance spectra of (a) free TiO_2 and (b) PANI/ TiO_2 composite (II).

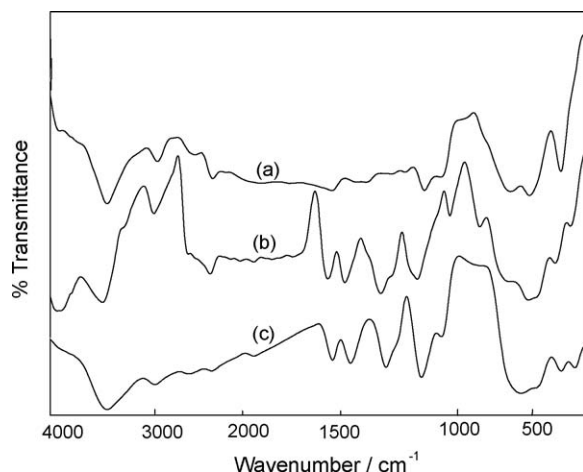


Fig. 4. FTIR spectra of (a) TiO₂, (b) free HCl-doped PANI and (c) PANI/TiO₂ composite (II).

of PANI. They are shifted after introducing the TiO₂ to 1298, 1486 and 1580 cm⁻¹, respectively. The peak of N–H stretching at 3488 cm⁻¹ of PANI is shifted to 3427 cm⁻¹ in the case of PANI/TiO₂ composite. This indicates that the hydrogen bonding in the polyaniline becomes stronger due to the formation of PANI/TiO₂ composite and therefore strong interaction may exist between the polyaniline and TiO₂ [28,29].

3.1.4. TGA

The thermal behavior of the two composites (II,X), prepared in the absence and presence of anionic surfactant, sodium dodecyl sulfate (SDS), is shown in Fig. 5. The weight loss between 25 and 150 °C shown in curves (a) and (b) is due to the expulsion of water molecules retained in polymer matrix. Between 150 and 300 °C the elimination of interaction between PANI and TiO₂ and also the dopant acid occurs. The strong weight loss detected in curve (b) between 150 and 300 °C may be ascribed to the removal of SDS species, which is an additional dopant counter ion in the PANI chain of the composite. The gradual loss of weight above 300 °C for the two samples indicates the skeletal degradation of polymer chain structure [30], which is completely decomposed at ca. 600 °C [14], confirming the good thermal stability of PANI below this temperature.

3.2. Spectral changes during the composite/dye interaction

Soon after the dye solution was added to the composite sample, the color of dye solution starts to disappear with time.

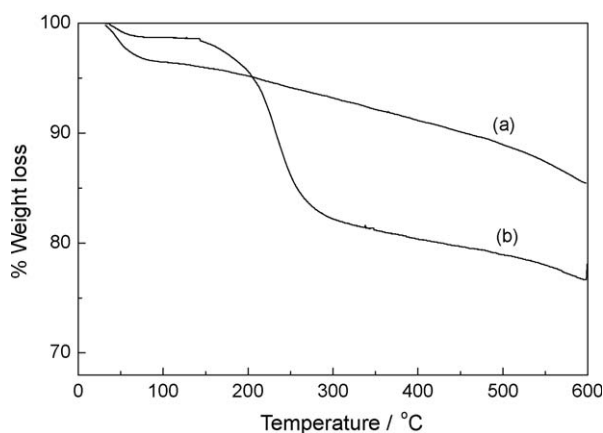


Fig. 5. Thermograms of PANI/TiO₂ composites prepared in (a) absence of SDS (composite II) and (b) presence of SDS (composite X).

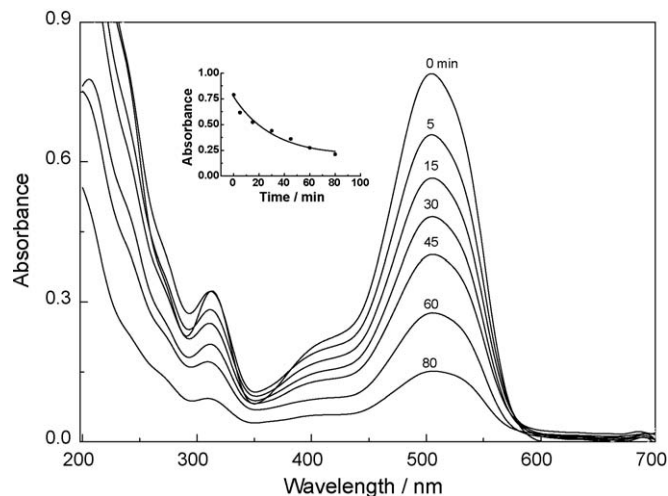


Fig. 6. Absorbance traces of ALR with time at 30 °C. [ALR] = 4×10^{-5} M, composite (II) = 0.05 g.

Such disappearance of color was accompanied with obvious decrease in the intensity of absorption peaks characteristics of the dye in both the UV and visible regions, Figs. 6 and 7. In general, the absorption peaks at 502 nm for ALR and 414 nm for QY correspond to the $n-\pi^*$ transitions of azo ($-N=N-$) group and quinonoid segment of ALR and QY, respectively, which are responsible for dye colors. The decolorization of the dye is therefore caused by the electrophilic cleavage of chromophoric bonds of the molecule. The absorbance of dyes in the UV-range refers to the $\pi-\pi^*$ transitions of benzene and naphthalene rings, which represent the aromaticity of the dye. The decrease in such absorption bands indicates the degradation of the dye molecule. Therefore, the change in absorbance in the visible region is taken as a measure for decolorization whereas the change of absorbance at the UV-region for degradation [31,32]. The simultaneous drop of absorption peaks in both regions of the dye spectrum demonstrates the increasing decolorization and degradation of the dye under these conditions. In the present kinetic study for the interaction of ALR and QY with PANI/TiO₂ composites, the measurements were restricted on monitoring the absorbance of each dye in the visible range which is considered a simple model for total degradation of the dye [33], particularly no colored intermediates were generated during the reaction as seen from the successive recorded spectra shown in Figs. 6 and 7. In

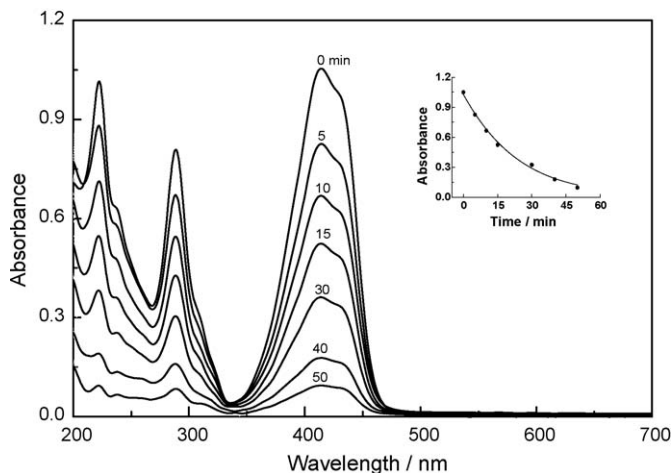


Fig. 7. Absorbance traces of QY with time at 30 °C. [QY] = 4×10^{-5} M, composite (II) = 0.05 g.

Table 1

Observed rate constants for different reaction systems at 30 °C. [Dye] = 4.0×10^{-5} M. Composite (II) is used.

System	Used mass of free PANI or PANI/TiO ₂ composite/g	$k_o (\times 10^{-4} \text{ s}^{-1})$	
		ALR	QY
Non-irradiated PANI/dye	0.017 ^a	1.88	2.60
Irradiated PANI/dye	0.017 ^a	2.00	2.78
Non-irradiated composite/dye	0.05	1.92	2.65
Irradiated composite/dye	0.05	3.22	4.57

^a This mass of PANI is equivalent to the mass of PANI in 0.05 g composite sample.

order to investigate further the reactivity of such composite/dye systems, the following factors affecting reaction rates have been studied.

3.3. Factors influencing the composite/dye interaction

3.3.1. UV-irradiation

In order to investigate the effect of UV-irradiation on the composite/dye interaction, three sets of experiments were carried out. The first set involves the interaction of free PANI with the dye both in the absence and presence of UV-light. A slight change in the rate constant was observed upon irradiation, Table 1. In the second set, two experiments were conducted under the same conditions without subjecting to the UV-light. One of them consists of free PANI (0.017 g) and the dye solution while the other involves the composite sample (0.05 g) with the dye solution. The amount of PANI in 0.05 g of the chosen sample of composite (II) was equal to that of free PANI (0.017 g). Since the reactions were taken place away from the UV-light, the TiO₂ in the composite sample is not expected to show any photocatalytic activity under these conditions. This is in fact our findings. The k_o -values derived from both the PANI/dye and composite/dye interactions are almost the same, Table 1. This indicates that the PANI present either in a free state or loaded on TiO₂ plays a significant role in dye removal. The third set of experiments was performed to study the effect of UV-irradiation on the composite/dye interaction. Two separate kinetic runs were carried out under the same conditions using 0.05 g of composite (II) mixed with the dye solution. In one of these runs the reaction mixture was illuminated with the UV-light whereas in the other was not. Upon illumination and though the light source has a little power (15 W), an enhancement in reaction rate was observed. The observed rate constants determined from the slopes of the linear regression plots of Fig. 8 for the non-irradiated and irradiated composite/ALR reaction systems were 1.92×10^{-4} and $3.22 \times 10^{-4} \text{ s}^{-1}$, respectively. For composite/QY system, similar behavior was observed with rate constants 2.65×10^{-4}

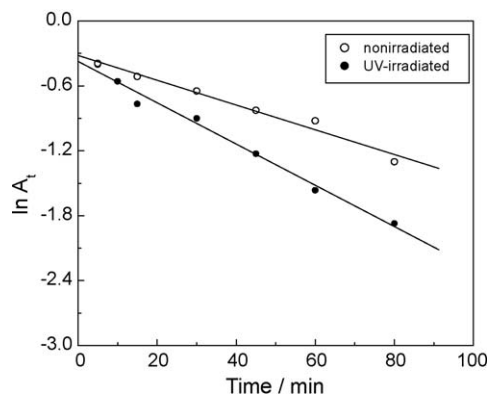


Fig. 8. First-order plot for the reaction of ALR with composite (II) in the absence and presence of UV-light at 30 °C. [ALR] = 4.0×10^{-5} M, composite = 0.05 g.

and $4.57 \times 10^{-4} \text{ s}^{-1}$, Table 1. Therefore, it can be concluded that ca. 70% increase in the reaction rate constant occurred for ALR and 72% for QY, owing to the photocatalytic property of the composite [20,21]. For this reason, all the kinetic measurements of the current study were performed under the UV-irradiation.

3.3.2. Effect of synthesis conditions

3.3.2.1. Amount of added TiO₂. A series of composites (I–IV) with variable amounts of TiO₂ (0.5–3.0 g) was prepared by keeping the concentrations of aniline, APS, and HCl fixed. Increasing the amount of TiO₂ produced composites of different PANI contents. The PANI content decreases on going from composite (I) to composite (IV) where the amount of TiO₂ increases from 0.5 to 3.0 g (Table 2). Since the operating composite sample entering the reaction with the dye solution was fixed at 0.05 g, then the PANI content of this sample would decrease at the same direction (I → IV). Such decrease in PANI content led to a decrease in reaction rate. Further evidence for this phenomenon may come from the strong ‘guest–host’ interaction such as hydrogen bonding between the TiO₂ and the polymer chain in the form NH...O–Ti [34]. The formation of H-bonding may render the composite activity less facile towards the reaction with the dye molecule.

3.3.2.2. Initial concentration of aniline. PANI/TiO₂ composites (V, II, VI, and VII) were prepared under different concentrations of aniline and fixed amount of TiO₂ (1.0 g). The derived k_o -values for the composite/dye interactions were found to increase with increasing the concentration of aniline involved, Table 2. This is attributed to

Table 2

Preparation conditions of PANI/TiO₂ composites, and the corresponding rate constants of composite/dye interactions. Composite (II) is the control sample.

Fixed conditions	Varied component	Composite yield (g) ^a	Composite number	$k_o (\times 10^{-4} \text{ s}^{-1})$	
				ALR	QY
[APS] = 0.058 M [ANi] = 0.061 M [HCl] = 1.26 M Poly.time = 1 h	TiO ₂ (g)				
	0.5	1.015	(I)	10.70	13.02
	1.0	1.408	(II)	3.22	4.57
	2.0	2.443	(III)	1.12	3.69
	3.0	3.437	(IV)	0.95	3.45
TiO ₂ = 1.0 g [APS] = 0.058 M [HCl] = 1.26 M Poly.time = 1 h	[ANi] (M)				
	0.031	1.193	(V)	1.12	3.02
	0.061	1.408	(II)	3.22	4.57
	0.122	1.521	(VI)	4.03	4.99
	0.173	1.747	(VII)	4.79	5.25
TiO ₂ = 1.0 g [APS] = 0.058 M [ANi] = 0.061 M [HCl] = 1.26 M Poly.time = 1 h	[SDS] ($\times 10^{-3}$ M)				
	0.0	1.408	(II)	3.22	4.57
	2.0	1.520	(VIII)	2.28	3.34
	5.0	1.670	(IX)	0.05	0.17
	8.0	1.775	(X)	0.05	0.06
	73.0	1.944	(XI)	0.06	0.05
TiO ₂ = 1.0 g [APS] = 0.058 M [ANi] = 0.061 M [Acid] = 1.26 M Poly.time = 1 h	Dopant acid				
	H ₂ SO ₄	1.456	(XII)	5.25	12.20
	H ₃ PO ₄	1.256	(XIII)	4.82	7.71
	HCl	1.408	(II)	3.22	4.57
	HNO ₃	1.464	(XIV)	2.83	2.87
TiO ₂ = 1.0 g [APS] = 0.058 M [ANi] = 0.061 M Poly.time = 1 h	[HCl]/M				
	0.27	1.675	(XV)	6.77	7.39
	0.74	1.580	(XVI)	5.54	5.17
	1.26	1.408	(II)	3.22	4.57
	1.75	1.375	(XVII)	2.41	3.67
TiO ₂ = 1.0 g [ANi] = 0.061 M [HCl] = 1.26 M Poly.time = 1 h	[APS] (M)				
	0.023	1.131	(XVIII)	1.76	3.02
	0.058	1.408	(II)	3.22	4.57
	0.116	1.642	(XIX)	5.54	9.37
	0.151	1.544	(XX)	4.82	6.17

^a The neat PANI formed = yield of composite – mass of TiO₂ initially involved.

the increasing content of PANI in the composites formed under these conditions.

3.3.2.3. Anionic surfactant. In this experiment, some composites have been prepared in the presence of SDS at variable concentrations $(2\text{--}73) \times 10^{-3}$ M. All other polymerization conditions were the same. These composites (VIII–XI) were employed to interact with dyes as described above. The rate constant decreased with the increase in the initial SDS concentration, Table 2. The composites led to a sudden drop in k_o -value from $2.28 \times 10^{-4} \text{ s}^{-1}$ to an average of $0.055 \times 10^{-4} \text{ s}^{-1}$ for ALR and from $3.34 \times 10^{-4} \text{ s}^{-1}$ to $0.055 \times 10^{-4} \text{ s}^{-1}$ for QY. The decrease in k_o may be due to the presence of SDS molecules as counter ions in the composite structure [35], which may retard the interaction of the dye with the composite. Incorporation of SDS anions into the backbone of PANI/TiO₂ can be confirmed by the increase in composite yield. As seen from Table 2 the higher the surfactant concentration the higher is the yield obtained. Such incorporation can be considered as an ionic interaction between SDS anions and the cationic centers in the polymeric structure while the polymerization takes place. Yavuz and GÖK [36] have reported that the PANI/TiO₂-SDS may be formed via (i) the TiO₂ nanoparticles get coated with the surfactant ions before they were incorporated into PANI, (ii) aniline can thus be polymerized onto the TiO₂-SDS system. Existence of surfactant into the polymerization medium of aniline in the presence of TiO₂ not only increases the solubility of reacting species in the solvent but also prevents the TiO₂ particles from aggregation. Such behavior of surfactant leads to the formation of high quality nanocomposite.

3.3.2.4. Type of dopant acid. The influence of various four different composites (XII, XIII, II, XIV) initially prepared in the presence of H₂SO₄, H₃PO₄, HCl, and HNO₃ on reaction rate was investigated. It was observed that the rate constant is strongly influenced by the type of composite, although the yield of all composites is fairly constant. Since the PANI in the composite is in its emeraldine salt form irrespective of the acid used, the variation of k_o may be derived from the differences in the size and nature of the dopant anion. As seen from Table 2, the k_o -values are classified in the decreasing order H₂SO₄ < H₃PO₄ < HCl < HNO₃. The anions of the polyprotic acids that doped in the PANI chain are HSO₄[−] and H₂PO₄[−] [37]. Cl[−] and NO₃[−] are the corresponding dopant anions for HCl and HNO₃. The activity of these composites may also depends on their crystallinity, particle size, and morphology [38].

3.3.2.5. Initial concentration of HCl. The effects of composites (XV, XVI, II, and XVII) prepared in the presence of variable concentrations of HCl (0.27–1.75 M) were investigated. Table 2 depicts the decrease in k_o with the increase in the initial concentration of the acid added to the polymerization medium. The decrease in k_o is thought to be due to the possible degradation of polyaniline that occurs during the polymerization process. The loss of composite yield observed with increasing HCl-concentration supports this phenomenon. These findings coincide with that reported in [39]. The degradation of polyaniline under these conditions may be due to the formation of either the over-oxidized polymer or the soluble quinone–hydroquinone structures [40,41].

3.3.2.6. Initial concentration of APS. The composites (XVIII, II, XIX, XX) prepared in the presence of variable concentrations of APS were tested via the reaction with the dye. The k_o was found to increase with increasing the initial concentration of APS up to 0.116 M and thereafter decreased, Table 2. At this limit of APS concentration the APS/PANI molar ratio is 2. At this molar ratio the maximum amount of PANI formed onto the surface of TiO₂ is attained. When the molar ratio exceeds 2 the amount of PANI

formed decreases and consequently the value of k_o significantly drops. This behavior may be due to the over oxidation of the resulting polymer by the present excess of APS, or the oxidative degradation of the earlier formed PANI on the surface of TiO₂ [42–46].

3.3.3. Composite/dye operating conditions

3.3.3.1. Composite loading. To study the effect of composite loading on the reaction rate of composite/dye system, the experiment was carried out at fixed concentration of the dye (4×10^{-5} M) and variable mass of composite. The rate constant was directly proportional to the composite mass, Fig. 9. This may be interpreted in terms of subjecting the dye to more active sites encountered for PANI and TiO₂ in the composite sample.

3.3.3.2. Initial dye concentration. The effect of dye concentration on the degradation rate was studied by keeping the mass of composite constant at 0.05 g while the concentration of the dye varies in the range $(0.5\text{--}8.0) \times 10^{-5}$ M. Within this concentration range the reaction still obeys first-order kinetics with respect to the dye concentration. It can be inferred from Fig. 10 that the rate constant decreased with the increase in dye concentration. The presumed reasons behind the decrease of k_o can be easily explained. The increasing coverage of the active sites of composite surface with the adsorbed dye molecules may shield the interaction of the composite with the precursor molecules. The UV-screening effect

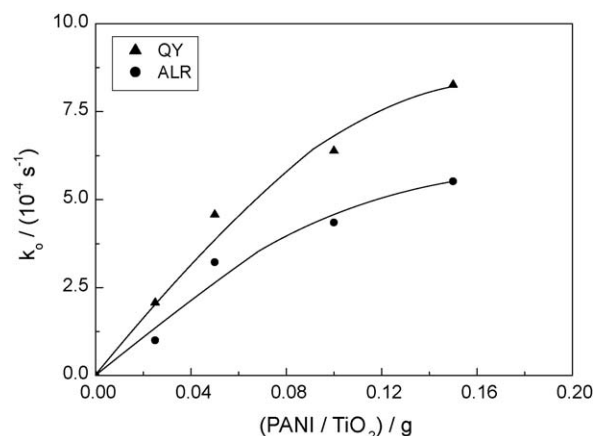


Fig. 9. Effect of PANI/TiO₂ amount on the rate constant for the reaction of dyes with composite (II) at 30 °C. [Dye] = 4.0×10^{-5} M.

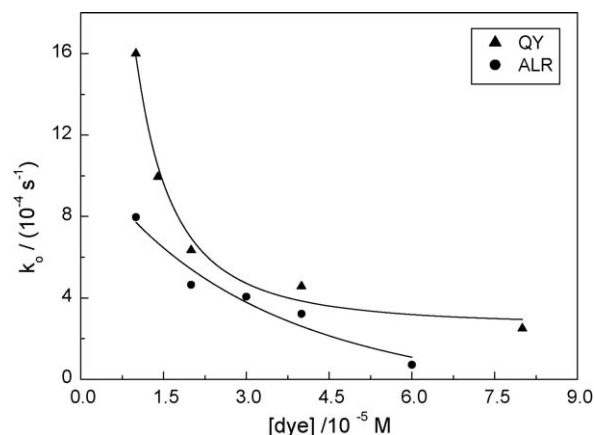


Fig. 10. Observed rate constant dependence on dye concentration for the reaction of dyes with composite (II) at 30 °C, composite = 0.05 g.

Table 3Specific rate constant and activation parameters for the reaction of dyes with composite (II). [Dye] = 4.0×10^{-5} M, composite (II) = 0.05 g.

Dye	Temp. (°C)	$k^a (10^{-3} \text{ s}^{-1})$ (pgdc) ^b	E (kJ/mol)	ΔH^\ddagger (kJ/mol)	ΔG^\ddagger (kJ/mol)	ΔS^\ddagger (J/mol K)
ALR	20	4.27	25.34	22.80	87.80	−211.08
	30	6.43				
	40	8.80				
	50	11.26				
QY	20	6.02	24.06	21.51	86.92	−212.37
	30	9.06				
	40	12.95				
	50	15.11				

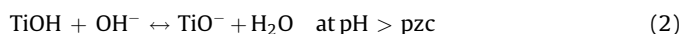
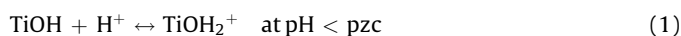
^a $k = k_o/m$, m is the mass of composite used.^b (pgdc) denotes per gram dry composite.

of the dye itself is another factor. At high concentration of the dye the UV-light may be significantly absorbed by the dye molecules rather than the penetration of photons into the composite surface. This results in less generation of OH^\bullet radical ($E_o = 2.81$ eV) that is the powerful species for the dye degradation [47,48].

3.3.3.3. Temperature. Composite (II) was chosen to react with the dye in order to investigate the effect of temperature on reaction rate. The temperature was varied within the range 293–323 K and the corresponding specific rate constant per gram dry composite (pgdc) was determined, Table 3. It is obvious that the higher the temperature, the faster is the reaction rate. Arrhenius plot constructed from $\ln(k)$ against the reciprocal of temperature (not shown) was linear with correlation coefficients 0.997 and 0.980 for ALR and QY, respectively. Arrhenius activation energy (E) and other activation parameters are depicted in Table 3. It is interesting to note that E values are somewhat higher than those of a diffusion controlled reaction ($10\text{--}21 \text{ kJ mol}^{-1}$) [49]. Therefore, they are characteristics of a chemical reaction control, not the diffusion control. Further scrutiny of Table 3 reveals consistent large and negative values for the entropy of activation (ΔS^\ddagger). This implies a highly ordered transition state (i.e. tight transition state) is involved in the composite/dye interaction.

3.3.3.4. pH. The pH of the reaction medium seems to represent one of the main parameters that affects the rate of reaction, particularly the dyes to be degraded may be found at different pHs in colored effluents. The pH dependence of reaction rate was examined in phosphate buffer solution of pH range from 2 to 10. The pH of buffer solution in acidic and alkaline ranges was obtained by adding a few drops of HCl (1 M) or NaOH (1 M). The

kinetic run was preformed by replacing the added water with the buffer solution. The dependence of k_o upon pH is represented in Fig. 11. The pH has strong inhibitory effect upon the kinetics of dye disappearance. Interpretation of such negative effect of the pH on the current composite/dye interaction is a very difficult task because of the possible contribution of both the TiO_2 and PANI in that effect. However, attempts have been made to explain this phenomenon. The pH-effect is related to the point of zero charge (pzc) of TiO_2 at pH 6.2 [50]. In acidic media (pH 6.2) the surface of TiO_2 is positively charged, whereas it is negatively charged under alkaline conditions (pH 6.2) [33,51] according to Eqs. (1) and (2),



Since ALR and QY are both negatively charged due to the sulfonated groups which are ionized in water, their electrostatic attraction to the composite surface is favorable in acidic solution, and forbidden in alkaline media due to the coulombic repulsion between the negatively charged surface of TiO_2 and the dye molecules. Thus, the reaction rate reached a maximum value at very low pH, Fig. 11. Moreover, the generation of OH^\bullet radicals by the effect of UV-light on the TiO_2 of the composite may also represent a further factor for increasing reaction rate in acidic environment [52]. In strong alkaline medium ($\text{pH} > 10$) such radical species are rapidly scavenged and therefore the reaction rate decreases [47]. Furthermore, because of the as-synthesized PANI part of the composite is in its emeraldine salt (ES) state due to the presence of dopant acid, this form of polymer interacts efficiently with the dye in the absence of buffer solution, Figs. 6 and 7. Incorporation of acidic buffer solution into the composite/dye system enhances the reaction rate, whereas the neutral and alkaline pHs may deprotonate the ES form, transforming the polymer chains into their emeraldine base (EB) form. If the EB form of polymer is inactive towards the interaction with the dye molecules, then the reaction will be inhibited in alkaline medium. This is in fact our findings. The rate constant decreases dramatically with increasing pH.

4. Mechanism

It is well known that the conduction band electrons (CBe^-) and valence band holes (VBh^+) are generated when the PANI/ TiO_2 composite is irradiated with the UV-light, which energy is greater than either the band gap of polyaniline (2.8 eV) or that of TiO_2 (3.2 eV). The CBe^- react with molecular oxygen to form superoxide radical $\text{O}_2^{\bullet-}$, which ultimately reacts with H^+ to produce HO_2^\bullet radical species. The photoinduced holes can react with water and the dye molecule (D) to yield hydroxyl radical and $\text{D}^{\bullet+}$ radical cations. All these oxygenous radicals ($\text{O}_2^{\bullet-}$, HO_2^\bullet , OH^\bullet) are powerful oxidizers capable to degrade the organic compound.

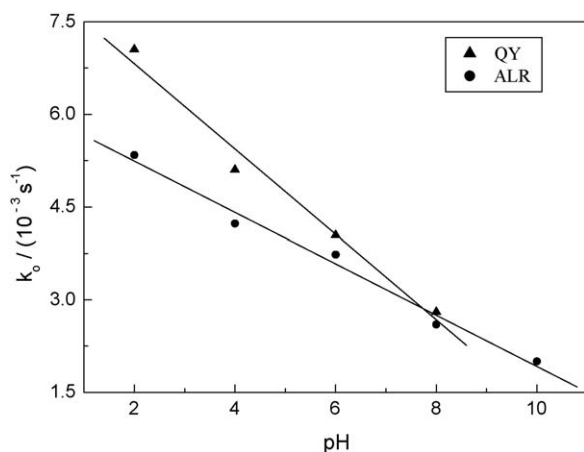
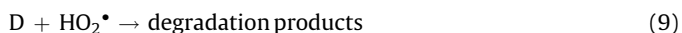
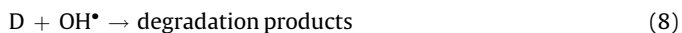
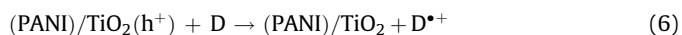
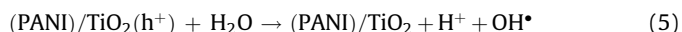
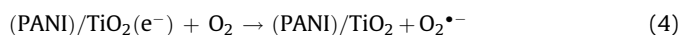
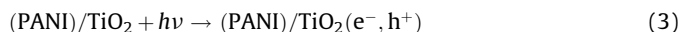


Fig. 11. pH dependence of observed rate constant for the reaction of dyes with composite (II) at 30 °C. [Dye] = 4.0×10^{-5} M, composite = 0.05 g.

Further, the reactive $D^{+\bullet}$ radical can transform into oxidation products. The high catalytic activity of the composite irradiated with the UV-light may come from the synergetic effect between the PANI and TiO_2 . Under UV-irradiation, both the PANI and TiO_2 absorb photons where the electrons generated by conducting PANI can be delivered into the conduction band of TiO_2 , enhancing the charge separation and the formation of oxyradicals. The photogenerated holes in the PANI species or in TiO_2 particles can migrate to the interface with the solution, which react directly with the surface-sorbed dye molecules to produce $D^{+\bullet}$ or indirectly through the OH^\bullet radicals to form degradation products [20,21,53]. Furthermore, the holes generated in the valence band of TiO_2 could also penetrate the PANI layer to reach the PANI–solution interface, promoting the oxidation of adsorbed substrate molecules. The relevant reactions illustrating the degradation process on the composite surface may thus be expressed as:



Without exposure to the UV-light, the observed photocatalytic activity of PANI/ TiO_2 composite described in reactions (3)–(10) is no longer operating, suggesting different route for dye removal. The lower values of k_o associated with the non-irradiated reactions in Table 1 provide a good evidence for this behavior. Since the TiO_2 does not have catalytic activity in the absence of UV-irradiation, the polyaniline could be the responsible partner to react with the dye molecules. Under these conditions, the decolorization of dye solution may be due to a chemical interaction of dye molecule with the positively charged polaron center ($-N^{+\bullet}-$) in the PANI chain [54]. However, further mechanistic study is required to fully elucidate this interaction.

5. Conclusion

Addition of PANI/ TiO_2 composite to the dye solution in the presence of UV-light led to the degradation of the dye. The degradation rate was obviously affected by two main factors, the synthesis conditions of the composites and the conditions of kinetics measurements. The composites responsible for high degradation rate are those prepared under [aniline] 0.173 M, [APS] 0.116 M, [HCl] 0.27 M, and TiO_2 0.5 g. The composite synthesized in the presence of H_2SO_4 is more efficient compared with those synthesized with H_3PO_4 , HCl, and HNO_3 . The presence of SDS yielded composites of very low activity. Regarding the conditions of kinetics measurements, the maximum rate was observed at [dye] $_0$ 1×10^{-5} M, composite amount 0.15 g, and pH 2. These optimum conditions may render the current method useful in treatment of colored water streams.

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